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SORPTION OF CADMIUM BY SOILS

Bruce E. Blom

Cold Regions Research and Engineering
Laboratory
Hanover, New Hampshire

June 1974

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13. ABSTRACT A brief review of the literature on cadmium in the environment, with emphasis on its role in soils and water, is presented. Experimentally, the interaction of cadmium with two soils and one naturally occurring zeolite was examined using calcium-saturated and potassium-saturated samples. The soils preferentially bound cadmium in the presence of either calcium or potassium with decreasing cadmium selectivity as the fractional cadmium surface coverage increased. Cadmium sorption was relatively higher with the potassium soils as compared with the calcium soils. For the loamy fine sand this increase was accounted for by electroselectivity principles, while such reasoning was inadequate to explain the increases observed with the Charleton loam sample. The preference for cadmium over calcium, as measured by the selectivity coefficient, was higher for the sandy soil. The zeolite was found to be calcium-selective. A method for monitoring the flow of cadmium through soil columns was examined. The use of spatial filtering, involving Fourier transforms, was found to be a suitable technique for monitoring the changes in cadmium concentration as it flows through soils. The experimental technique involves the use of gamma-emitting metal		

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isotopes in conjunction with an external scintillation counter; thus the soil column remains undisturbed and may be used for several experiments.						
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SORPTION OF CADMIUM BY SOILS

Bruce E. Blom

June 1974

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PREFACE

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SUMMARY

Cadmium is efficiently adsorbed by two acidic soil horizons in the presence of a relatively large excess of calcium or potassium. The adsorption is not completely reversible and the amount desorbed may possibly decrease with time as isomorphic substitution progresses. Nevertheless, the apparent separation factor provides a good measure of the efficiency of the adsorption. It is fortunate that the adsorption of cadmium in these soils is irreversible, as it will be less likely that this metal will be desorbed in the presence of large amounts of other counterions. The mechanism by which cadmium is held irreversibly is not known; it seems to be unlikely that diffusion into particle interiors has had a chance to become significant over the time frame of these experiments. Clinoptilolite, although of value as an ammonium scavenger in wastewater treatment, has little significance for cadmium removal.

A method for monitoring the flow of radioactive cadmium through soil columns was examined. The use of spatial filtering, involving Fourier transforms, was found to be a suitable technique for monitoring the changes in cadmium concentration as it flows through soils. The filtering function is seen to be useful in decoding convolved profile data obtained by the described methods. Problems exist in the high frequency region but can be corrected for, and excellent agreement is obtained in the low frequency region (the descending part of the curve). The latter is of more interest from a theoretical standpoint. The method is quite general and should work with other system geometries and other isotopes whose photon energies are so high as to give poor resolution.

SORPTION OF CADMIUM BY SOILS

by

Bruce E. Blom

INTRODUCTION

Concern over pollution of the environment by cadmium has grown in recent times as more and more researchers have begun studying the effects and fate of cadmium in the air, the waters (both fresh and salt), the earth, and the human body. The most extensive research has been performed by medical researchers who have investigated the toxicology of cadmium, interest in which was stimulated by cases of acute cadmium poisoning in certain areas of Japan.⁴¹ Poisonings on a large scale have not occurred in the United States in any known area, although local contaminations have occurred.⁴² Medical research is also concerned with the cumulative effect of cadmium on a long-term basis, especially in light of the increasing use of cadmium in industrial processes.

The increasing use of spray irrigation on land, as well as other techniques utilizing the land for waste effluent treatment, have resulted in growing concern over the consequences of such practices. The investigations described in this report were undertaken to give a better understanding of the interaction of cadmium, a potentially dangerous pollutant, with soils.

The report is divided into three parts:

- I. Sources and effects of cadmium in the environment: a brief review
- II. The interaction of cadmium with some native New Hampshire soils
- III. The flow of cadmium through soils: an experimental method

I. SOURCES AND EFFECTS OF CADMIUM IN THE ENVIRONMENT: A BRIEF REVIEW

This section discusses the role of cadmium in general. Its chemistry in fresh water and soil is treated in more detail. Certain areas are extensively reviewed by Lagerwerff.²⁴

Sources of cadmium

Cadmium enters the environment from many sources. It is always associated with zinc: the standard zinc slab at the National Bureau of Standards contains approximately 1/2% cadmium (ref. 38, p. 1). It enters the air with emissions from zinc, copper and lead smelting plants. It can be leached from the zinc coating on galvanized iron pipe used in older plumbing, and from plastic plumbing also, as cadmium is used as a thermal stabilizer in polyvinylchloride, the most common plastic used for plumbing purposes.¹⁵ Cadmium is a waste product in spent liquors from numerous

SORPTION OF CADMIUM BY SOILS

Table I. Cadmium and zinc in the geosphere, hydrosphere and biosphere (from Schroder;¹¹ data from Bowen¹²).

	Cd (ppm)	Zn (ppm)	Ratio Zn:Cd
Sea water	0.00032-0.00075	0.009-0.021	28
Marine plants	0.4	150	375
Marine animals	0.150-3.0	6-1500	40-500
Fresh water	0.08	0.01	0.13
Soil	0.06	50 (10-300)	833
Land plants	0.6	100	167
Insects	+	400	?
Mammals	0.5	160	320
Igneous rocks	0.2	70	350
Shales	0.3	95	317
Sandstones	0.05	16	320
Limestones	0.035	20	571
Coal	+	40-108	?
Coal ash	50	10,000	200
Petroleum	0.24-0.54	0.32 (0.03-8.1)	
Fertilizers	1.0-10.0	130-2500	130-250
Air ($\mu\text{g}/\text{m}^3$)	0-0.37	0-1.7	37-48

electroplating operations. It also appears in some batteries, pesticides, fungicides, fertilizers, paints, alloys and dyes. It is found in automobile tires as a result of the zinc compounds used in the vulcanization process.¹³ Some plants can take up cadmium from the soil in which they are grown; this may explain why cigarette smoke contains significant amounts of cadmium (ref. 11, p. 24; ref. 31).

Clearly, the sources of cadmium are numerous. The distribution of cadmium and zinc on the earth is shown in Table I. Hem¹⁴ suggests that a considerable amount of the cadmium utilized in the United States (6000 metric tons in 1960) and worldwide (17,000 metric tons) may escape into the environment, although it is difficult to prove such a contention because of the lack of available data.

Health aspects of cadmium pollution

There is considerable information dealing with acute cadmium poisoning. Sufficient evidence exists to indicate that cadmium is accumulated primarily in the kidneys with smaller accumulations in the liver. Although chemically similar to zinc, cadmium has no known function in any of the life forms studied. Schroder¹⁵ reports having raised mice on cadmium-free diets with no adverse effects. Since zinc is utilized by the body it is a possibility that, because of chemical similarity, cadmium competes with zinc in some of its metabolic functions, causing some form of cadmium poisoning. The toxicity of cadmium is approximately $\frac{1}{10}$ to $\frac{1}{2}$ that of methylmercury, the most toxic form of mercury. Although acute cadmium poisoning is one potential problem, it has also been suggested^{16, 17} that smaller amounts of cadmium can give rise to hypertension.

The route by which cadmium enters the body appears to be extremely important. Evidence indicates that approximately 40% of the cadmium entering the body via the respiratory system is absorbed, while only about 10% is absorbed from the gastrointestinal tract. The remaining 30% of the cadmium entering the body via the respiratory system is excreted in the urine.

retained within the body, whereas less than 10% of that ingested into the gastrointestinal system is retained (ref. 11, p. 30). Thus, airborne concentrations of cadmium do not have to be as high as aqueous concentrations to achieve the same effect within the body.

For further information on the various physiological effects of cadmium the reader is referred to two major reviews.^{11 30}

Air pollution by cadmium

Buchauer⁴ conducted extensive tests on soils and vegetation in the vicinity of a zinc smelter. Cadmium emitted from the smelter was primarily in the form of cadmium oxide particulates. Ninety percent of it was found in the top 15 cm of soil with up to 1500 ppm in the surface horizons (A_0 and A_1 ; < 2 mm particle size). Cadmium levels decreased from approximately 1200 ppm in the vicinity of the plant to about 17 ppm 24 km to the east. The amount of water-extractable cadmium decreased with increasing soil pH and the toxicity of the soil to plants could be reduced by the application of 4 tons/acre of lime. It is estimated that the smelter emitted between 0.08 and 0.10 ton of cadmium per day during 1970. The greatest emissions apparently occurred after sintering of ores began (1949) but before an electrostatic precipitator was installed (1953). Estimated emission of cadmium during this period was approximately 0.45 ton per day.

Studies in Sweden (ref. 11, p. 19) in the vicinity of a copper-cadmium alloy plant showed a monthly mean value for cadmium oxide particulates of $0.6 \mu\text{g}/\text{m}^3$ with a high value of $5.4 \mu\text{g}/\text{m}^3$ for a 24-hour period. In contrast, concentrations of cadmium oxide in rural areas were found to be of the order of $10^{-3} \mu\text{g}/\text{m}^3$. The maximum permissible limit for workers in contact with cadmium oxide fumes is $100 \mu\text{g}/\text{m}^3$ (ref. 38, p. 33; ref. 24). In a study of urban air in Cincinnati²⁷ 40% of the total airborne cadmium was in the form of particles less than $2 \mu\text{m}$ in diameter.

Air pollution by cadmium is obviously a "local" problem due to the relatively limited range of cadmium oxide particles. Direct poisoning by inhalation depends on particle size, concentration, and duration of exposure. The problem may be spread beyond the local area however, as a variety of plant species are able to extract cadmium from the soil. Wheat and rice are significant examples (ref. 11, p. 24).

Water pollution by cadmium

Cadmium concentrations were recently determined in waters throughout the United States.⁹ Hem¹⁵ reviewed these data and found that, as expected, cadmium concentrations are highest around industrial centers. Of the approximately 720 sites sampled, only 43 equalled or exceeded the current Public Health Service limit of 10 ppb; 11 were public water supplies (raw) and 27 were located in the southeastern region of the country. It should be noted that all samples were taken at approximately the same time of the year and do not necessarily reflect a permanent condition. The highest value reported was 130 ppb in a small creek in Arizona.

Studies have also appeared on the distribution of cadmium in the oceans. Windom and Smith found cadmium in continental shelf water, sampled in the upper 5-10 m, to average about 0.1 ppb.⁴⁰ Ashton et al.,¹ using deep sea cores, found the average cadmium concentration of the sediment to be 225 ppb (range of 40-580 ppb). There appeared to be no significant increase in concentration of cadmium in shell material over that found in the clayey matter.

It is difficult to say whether simple compound formation and dissolution are significant in controlling the amount of soluble cadmium in waters. There are insufficient data available describing aquatic systems where several other variables, such as organic matter, have been measured in addition to the usually measured pH and amounts of carbonate.

SORPTION OF CADMIUM BY SOILS

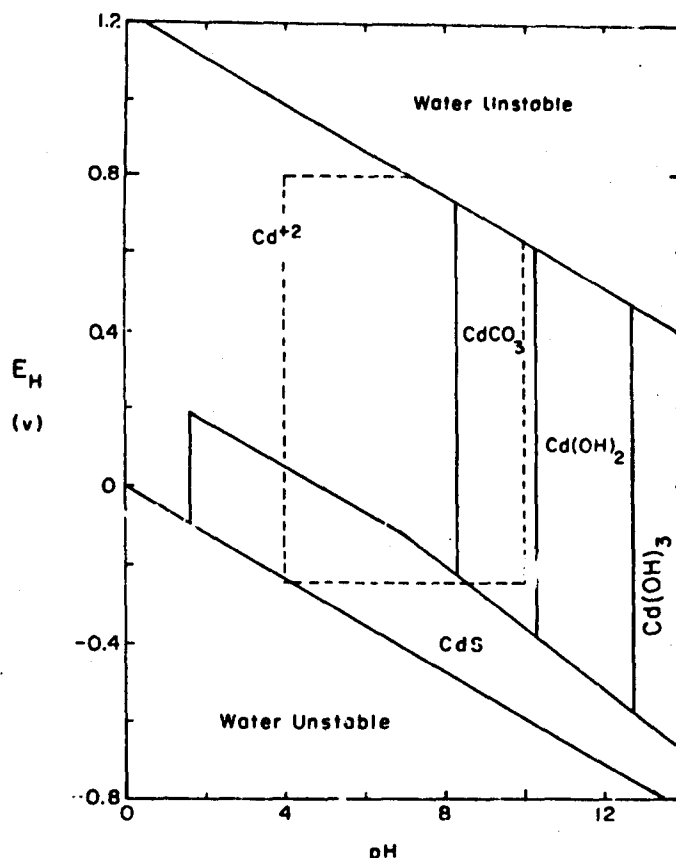


Figure 1. E_H vs pH stability field diagram for the system $Cd-CO_2-S-H_2O$ at $25^\circ C$ and 1 atmosphere. (From Hem.¹⁵) Cadmium concentration = $10^{-7} M$, dissolved carbon dioxide and sulfur = $10^{-3} M$. The solid lines represent phase boundaries where the indicated species are stable. The dashed line encompasses the area of conditions that would almost always be found in nature. Under anaerobic conditions (small or negative E_H) sulfate can be reduced to sulfide.

In order to determine the form and extent of cadmium in waters at least approximately, it is important to know the effect of carbon dioxide and pH on solubility and solid formation of cadmium. Hem¹⁵ treated the $Cd-CO_2-H_2O$ system as having constant CO_2 content; the resultant stability field and solubility diagrams are shown in Figures 1 and 2, respectively. The effect of the partial pressure of carbon dioxide on the formation of solid phases is shown in Figure 3. Whether it is justifiable to have the system closed with respect to CO_2 (i.e. constant total carbonate concentration) is debatable. In such an open system ($P_{CO_2} = 10^{-3.5}$ atm) it is unlikely that cadmium hydroxide will ever be formed. The effect of chloride in either the closed or open system is negligible at the maximum permissible value of 250 ppm. Above 370 ppm, chloride will begin to increase the maximum pH for cadmium solubility. This is due to the fact that cadmium forms stable chloro-complexes.⁵ The effect of activity coefficients, which is shown in the original paper,¹⁵ is such that an increase in ionic strength increases the solubility of cadmium.

There are two other likely mechanisms that are potentially capable of controlling soluble cadmium. The first of these is the formation of metal-organic complexes. Morel and Morgan^{12, 11} analyzed multicomponent metal-ligand systems by solution of the equilibrium equations. In one system

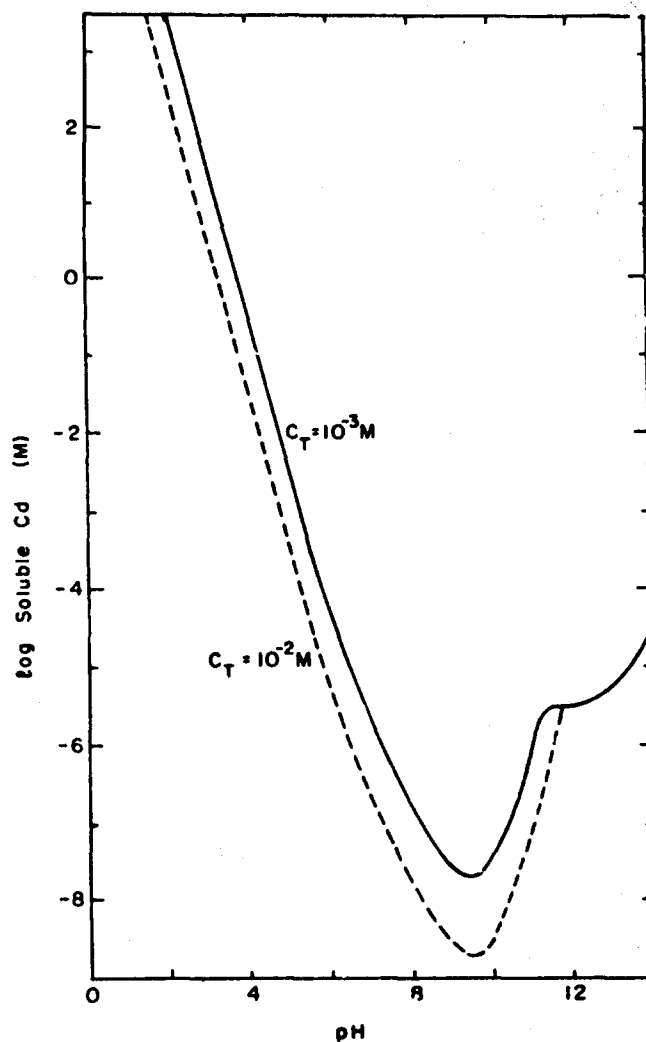


Figure 2. Solubility of cadmium as a function of pH. (Data from Hem.¹⁵) The system is closed with respect to carbon dioxide at a total concentration of 0.001 M (or 0.01 M as shown). The increase in solubility is due to the formation of hydroxo-complexes and the higher solubility of cadmium hydroxide itself versus cadmium carbonate.

(pCd = 9)* that did not take Cl^- into account approximately 20% of the cadmium was present as the nitrilotriacetate (NTA) complex (pNTA = 6), 70% as the free metal, and 10% as the sulfate. In their more expanded system involving 20 metals and 31 ligands at pH = 8, with initial values of pCd = 6, pCl = 0.3 and pNTA = 7, very little of the Cd-NTA complex was formed as the cadmium was bound almost exclusively to the chloride in various degrees of complexation. Maljkovic and Branica³⁰ investigated the Cd^{+2} - Ca^{+2} - Cl^- -ethylenediaminetetracetate (EDTA) system polarigraphically and found that, as expected, the formation of CdCl^+ as well as calcium-EDTA complexes decreased the amount of Cd-EDTA complex formed. However, of significant importance were results obtained with the following solutions:

* pCd = $-\log[\text{Cd}]$.

SORPTION OF CADMIUM BY SOILS

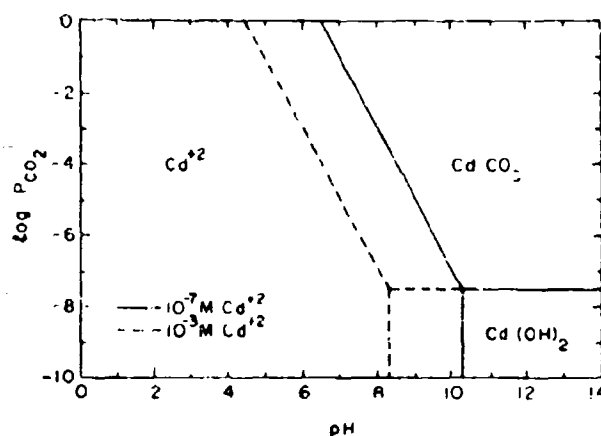


Figure 3. Stability of the hydroxide and carbonate of cadmium as a function of the partial pressure of carbon dioxide. (Data from Butler.⁵)

A. $p_{Cd} = 6.4$ $p_{Cl} = 0.23$ $p_{EDTA} = 6.1$

% ionic cadmium after 24 hours = 0.

B. $p_{Cd} = 6.4$ $p_{Cl} = 0.23$ $p_{Ca} = 2$ $p_{EDTA} = 6.1$

% ionic cadmium after 24 hours = 75.

C. $p_{Cd} = 6.4$ $p_{Cl} = 0.23$ $p_{Ca} = 1.4$ $p_{EDTA} = 6.1$

% ionic cadmium after 24 hours = 100.

Example B represents an initial Ca/Cd ratio of 2.5×10^4 .

Thus it is apparent that although calcium could be present in great excess over cadmium it is still possible for a substantial portion of the cadmium to be complexed.

Other organic ligands may be expected to play a significant role in cadmium control. However, the data are insufficient to ascertain which ligands are important and to what extent they will be found in natural water systems. Formation of soluble complexes could lead to waters carrying higher levels of cadmium than predicted on the basis of inorganic solubility data.

Another mechanism is that proposed by Jenne¹⁹ where it is assumed that hydrous oxides of manganese and iron sorb heavy metals. Jenne cites evidence for this type of mechanism in a number of cases but the exact nature of the mechanism is elusive and may be highly dependent upon the particular cation being sorbed and the presence of other constituents in the system. Colloidal particles containing such metals might well be expected to pass through the 0.45-micron filters used in water quality work and thus leave the metal available for detection. Unless such a suspension is destabilized, metals associated with colloidal particles are in essence still soluble. On the other hand if a stable suspension is not formed then hydrous oxides may become incorporated into sediments, thereby removing the metal from solution. Schroder (ref. 38, p. 3) reports that sediment mud near a battery manufacturing plant on the Hudson River contained 24% cadmium whereas the surrounding water contained only 2 ppm of cadmium.

Cadmium in soils

Lagerwerff and Brower¹⁴ studied the exchange of cadmium on three different soils varying in clay content and type, and found the exchange to be normal (with regards to electroselectivity) with calcium- and aluminum-treated soils but abnormal with sodium-treated soils. For the latter, they attributed the decreasing amount of cadmium adsorbed with decreasing sodium chloride concentration as being due to a decreasing soil exchange capacity caused by the adsorption of aluminum compounds on the samples during their preparation.

John¹⁰ used 30 surface soils and measured the adsorption isotherms using solutions containing 1-1000 ppm cadmium. The data were fitted with Langmuir adsorption isotherms and adsorption maxima for all soils correlated with aluminum and zinc soluble in 0.01 M calcium chloride. John et al.¹² also studied the effect of cadmium on the growth of radish and lettuce plants, using 30 surface soils. Three variables significantly contributing to the uptake of cadmium into the plants included the ability of the soil to adsorb cadmium, the amount of acetate-extractable cadmium in the soil, and the amount of organic matter. The level of cadmium used in these soils was 100 ppm, which is higher than is normally found but is not unreasonable compared with the level in contaminated areas.

In another study John et al.¹¹ found high cadmium concentrations in oat roots with small amounts in the aboveground portions. Application of carbonate, nitrate, chloride, sulfate, and phosphate salts of calcium decreased cadmium percentage in the plant root system but not in the upper portions of the plant. Page et al.,¹³ using solution culture techniques, studied the effect of cadmium, in the ranges of 0.1 to 10 ppm, on the growth of corn, turnips, beets, beans, tomatoes, cabbage, lettuce, green pepper and barley. The results were dependent on the type of plant, beets, beans and turnips being most susceptible while cabbage was the most tolerant.

Buchauer,⁴ investigating the effects of airborne cadmium on vegetation and soils, found varied tolerances among the local vegetation. Lehman and Wilson,¹⁵ using 8-ft-deep field lysimeters and effluent from a treatment plant, reported an unspecified amount of cadmium in the effluent but no detectable amount of cadmium in the filtrate. Bermuda grass clippings from the site contained 3.6 mg cadmium per 100 g dried grass. Whether this is a high value relative to the soil cadmium concentration is unknown. Lagerwerff and Specht¹⁶ analyzed plants growing alongside well-traveled roads and detected higher than normal amounts of cadmium which presumably had come from automobile tires. Klein¹⁷ sampled 264 surface soils over a 300-square-mile area and found for various land usages mean cadmium concentrations increasing in the order: residential < agricultural < industrial < airport. The mean values ranged from 0.41 ppm to 1.17 ppm with standard deviations approaching 100% of the mean values.

All available data indicate that cadmium applied to the surface of soil remains in close proximity to the surface, either having been precipitated or immobilized by chelation or adsorption. Many plants can take up this cadmium and pass it into the food chain.

Effect of cadmium on sewage treatment processes

Comparatively little work has been done on the effect of cadmium on sewage treatment processes. Mosey¹⁸ studied the effect of cadmium on anaerobic digestion and found that, as is the case with other heavy metals, sulfide and carbonate formation are responsible for low cadmium toxicity with respect to biological processes. Above pH = 7, carbonate formation appears to be the responsible mechanism of cadmium precipitation whereas sulfide formation is effective below this pH. The toxic effect of cadmium is found to be fast acting and the addition of sulfide did not entirely prevent it. Sulfide has to be present before the cadmium is added in order to prevent the inhibition of the biological processes. Optimum results were obtained with equimolar concentrations of sulfide and cadmium.

Since most sewage treatment processes in use today operate under aerobic conditions, cadmium sulfide precipitation is not an important factor but carbonate formation can still take place under these conditions. Since most systems have some method of agitation, the sewage solution should remain saturated with CO_2 . Thus at a pH = 7, the maximum amount of soluble cadmium should not rise above approximately 26 ppm. However, at pH = 6, this maximum value can be as high as 2600 ppm, indicating pH control is critical. Polish workers¹² have found that the maximum permissible amount of cadmium (in the form of sulfate) is 0.8 ppm for activated sludge processes. At about this value cadmium begins to interfere with the chemical and biological processes taking place.

Carbonate formation is a factor in cadmium removal but it is not necessarily the predominant mechanism nor even a significant one (except for high concentrations of cadmium). In one study,⁹ chromium, copper, zinc and nickel were studied, to determine their effect upon the biological processes, both singly and in combination, when they were incorporated into an influent stream that was fed to activated sludge digesters. In single ion experiments concentrations usually ranged from 2 to 20 ppm. Based upon the solubility of the simple carbonate and hydroxide species only zinc could be effectively removed. Copper and nickel would remain in solution. However, the concentrations of the metals used in these experiments did decrease by varying amounts. The majority of the metal in this case was removed by interaction with the microbial floc in the digester. Metals in combination exerted no synergistic effect.

II. THE INTERACTION OF CADMIUM WITH SOME NATIVE NEW HAMPSHIRE SOILS

Introduction

In order to obtain more information on the interaction of cadmium with soils, a series of laboratory experiments, under equilibrium conditions, were performed utilizing soil samples from the lysimeter phase of the CRREL Wastewater Management Project. Two other materials were also studied: Charleton loam, a more acidic soil than the others studied, and clinoptilolite, a naturally occurring ammonium-selective zeolite which has potential use in wastewater treatment.

In vitro studies of this type represent approximations to actual in situ conditions. Natural systems exist in dynamic equilibrium and/or nonequilibrium states and as such cannot be readily explained except in generalities. Equilibrium studies provide a clearer understanding of some of the processes taking place in natural systems.

Materials and methods

Samples of the A and B horizon of a Windsor loamy fine sand collected from a site near the Lebanon Regional Airport, Lebanon, New Hampshire, were used. Both horizons have water pH's of approximately 6. The A horizon consists of approximately 75% sand with the remainder of the material equally divided between silt and clay. The B horizon contains 86% sand with the remainder again equally divided between silt and clay. A Charleton loam (obtained from the Robert Adams property, Etna, New Hampshire) was selected because of its higher clay content (approximately 25%) and its acidic properties; pH's of 1:1 soil-solution mixtures in 0.01 M calcium chloride were approximately 4.7. The predominant exchangeable cation in both soil types is calcium. The clinoptilolite sample (W.R. Grace & Co., Sample #6787-24-#2, attrition index of 10) originated from altered trachytic tuff volcanic deposits and consisted of > 85% clinoptilolite with minor amounts of quartz, glass, mordenite and montmorillonite. It was slightly basic in calcium chloride solutions. Additional data on clinoptilolite may be found in a study by Hower.¹³ In all cases the < 2 mm fractions were used and, in the case of the soils, root material was removed.

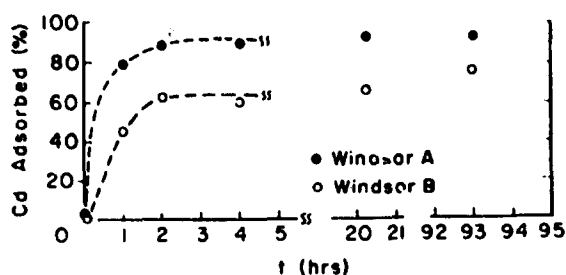


Figure 4. Cadmium adsorption on Windsor A and B soils as a function of time.

All samples were calcium-saturated by passing 0.4 M calcium chloride (pH = 6.1) through the soil columns until constant calcium concentrations were obtained in the leachate. In addition, potassium-saturated soils were prepared using 1 M potassium chloride (pH = 5.9). Deionized distilled water was passed through the column until the washings showed a negative silver nitrate test.

Cadmium chloride solutions were prepared by serial dilution of stock solutions prepared from the reagent grade salt and were spiked with carrier-free ^{109}Cd (International Chemical and Nuclear

Corp. #61006). The solutions were acidic (pH = 4.3) because the spike was 0.5 N in HCl. Cadmium solutions were prepared ranging from $5 \cdot 10^{-7}$ N (27 ppb) up to 10^{-2} N; they were stored in acid washed polyethylene bottles. For the higher concentrations, total cadmium plus calcium was constant at approximately 10^{-2} N.

Equilibration of samples with cadmium solutions at the highest concentrations was carried out in polypropylene centrifuge tubes at room temperature (-22°C) using 1-g samples and 10 ml of solution. All other isotherm data were obtained using 5-g samples and 25 ml of solution. After sufficient time for equilibration (approximately 48 hours; see Fig. 4) the samples were centrifuged and supernatant pH and activity were measured, the latter with a scintillation counter (Nuclear-Chicago Model #8703 with Model #821330 NaI-Tl well probe). As a check, the samples were washed with water and isopropanol until the supernatant liquid showed no activity and the activity of the soils was measured. A comparison of the amount of cadmium associated with the soil complex as determined directly and indirectly showed no significant difference. Negative adsorption therefore appears to be of no importance. Consequently, later experiments were performed measuring only the supernatant activity. Cadmium exchange capacities were determined using 0.1 N CdCl_2 (pH = 5) spiked with high specific activity ^{109}Cd (ICN #62004). One gram of soil and 30 ml of solution were placed in a centrifuge tube and shaken for 1 hour; five repetitions of this procedure were found sufficient to ensure saturation of the samples. All samples were run in duplicate except for the Windsor A which was run in triplicate. The amount of cadmium associated with the soil was determined by direct counting of the soil.

Results and discussion

Figure 5 shows the exchange isotherms at highest cadmium concentrations for some of the samples. The Charlton samples exhibit some interesting behavior. The surface horizon shows what is known as selectivity reversal; this is indicated by the S-shaped isotherm. Such reversal is usually attributed to differences in the size of the competing ions or to the presence of two different types of exchange sites, the total isotherm being a composite of the individual isotherms for each site. Since the radii of the two divalent ions are approximately the same ($r_{\text{Ca}} = 0.97 \text{ \AA}$, $r_{\text{Cd}} = 0.99 \text{ \AA}$), the latter may be the case for these soils as both inorganic and organic sites are competing for cadmium ions. The other two Charlton samples have isotherms indicative of a preference for calcium. Assuming that the clay type in all three horizons is the same, the preferential uptake of calcium by the clay and silt combined with what is apparently preferential binding of cadmium by the organic matter may give rise to the S-shaped isotherm for the surface horizon as seen in Figure 5. As the clay and silt constitute at least 50% of every horizon they must have a very low exchange capacity.

SORPTION OF CADMIUM BY SOILS

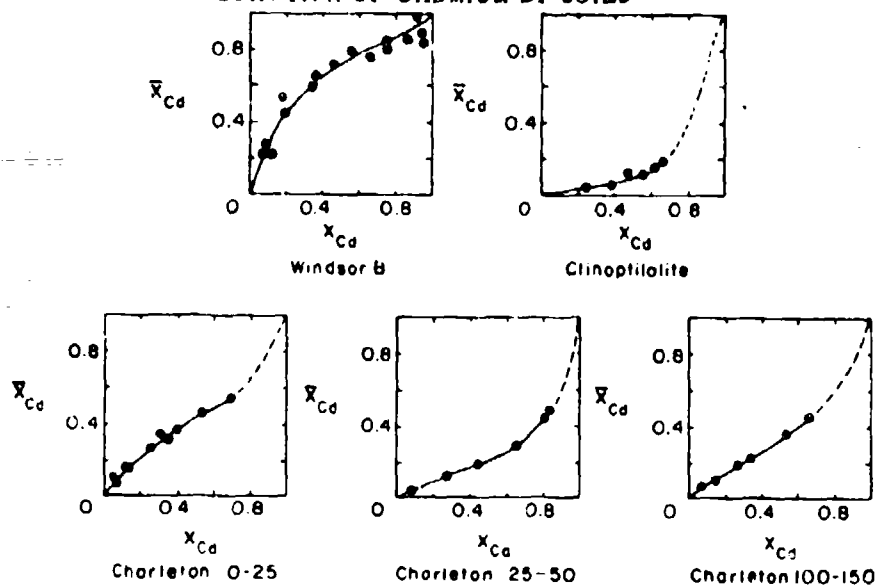


Figure 5. Exchange isotherms for the system $\text{Cd}^{2+}\text{-Ca}^{2+}\text{-soil}$. The barred quantities refer to the equivalent ionic fraction of cadmium associated with the soil complex. The abscissa represents the ionic fraction of cadmium in solution. The numbers following the designation "Charleton" refer to the depth in centimeters at which the sample was obtained. Total calcium plus cadmium in solution is constant (10^{-2} N).

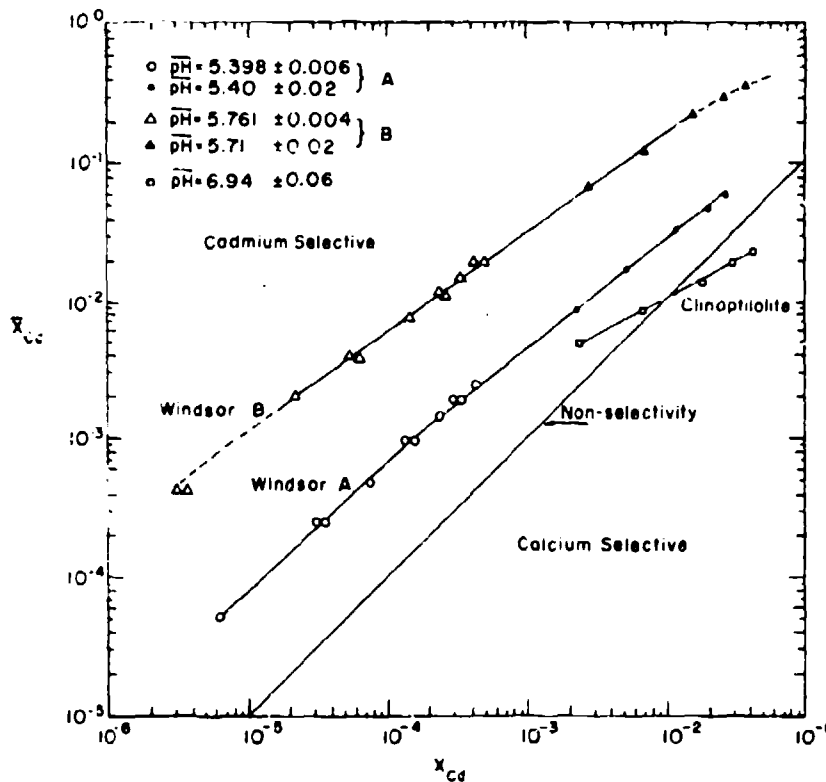


Figure 6. Cadmium exchange isotherms at low concentration in the presence of constant calcium chloride ($[\text{Ca}^{2+}] = 9.88 \times 10^{-3} \text{ N}$).

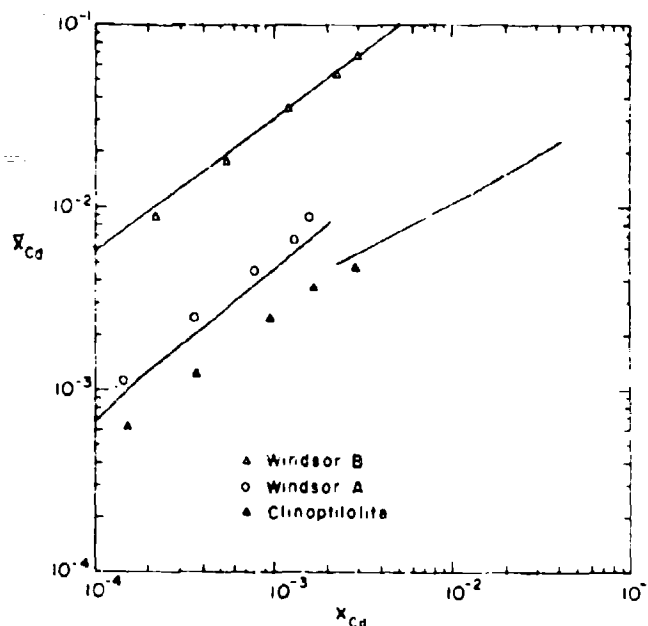


Figure 7. The effect of calcium chloride concentration on cadmium adsorption. The solid lines represent $[Ca^{+2}] = 9.88 \times 10^{-3} N$ and the points $[Ca^{+2}] = 9.88 \times 10^{-4} N$.

The Windsor B sample shows just the opposite behavior. It has a high preference for cadmium yet has an extremely low clay and silt content. Clinoptilolite shows a preference for calcium under these conditions. Howerly¹⁸ has investigated clinoptilolite using various other ion pairs and has found similarly shaped isotherms.

Figure 6 shows the adsorption isotherms for the samples over several orders of magnitude of surface cadmium coverage. The fact that the isotherms are linear would tend to imply that there are no detectable irregularities in the exchange sites at these surface coverages (the amount of extractable cadmium in the original soil samples was found too low to have an effect on the results). The position of the lines is very interesting. As will be seen shortly, the degree to which the lines are displaced from the line denoting non-selectivity is directly related to the magnitude of the separation factor. Thus the Windsor B, although having a lower exchange capacity and significantly less organic matter than the A horizon, is a more efficient "trap" for cadmium in the presence of calcium. In the case of clinoptilolite selectivity reversal is apparent.

Figure 7 shows the data obtained for two different calcium concentrations. For the Windsor B material and the clinoptilolite the effect of calcium concentration is minimal whereas for the Windsor A material there seems to be a definite effect. Increased adsorption with decreasing supporting electrolyte concentration has often been ascribed to the increased dispersion of the clay with decreasing ionic strength. This is due to the increased accessibility of the clay adsorption sites as the material becomes more dispersed. (This reasoning has also been utilized to explain the apparent irreversibility found in heterovalent ion exchange in soils.¹⁹) This would explain the A horizon results (although the slight difference in pH cannot be ruled out entirely) and also the B horizon results, the clay content of the latter being so small as not to manifest itself. The effect of pH on the ammonium ion capacity is shown in Figure 8. The results were obtained by saturating the soils with ammonium acetate buffers of varying pH values and removing any excess solution.

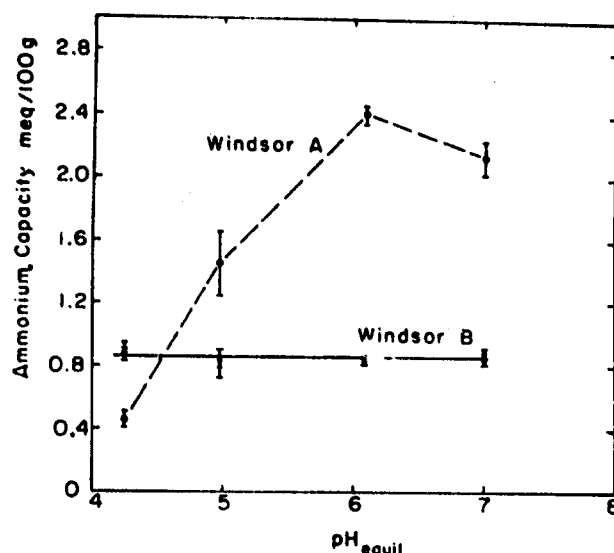


Figure 8. Ammonium ion capacity of Windsor soils.

(Such treatment resulted in colored leachates, the brownish-orange color increasing in intensity with decreasing pH. Atomic absorption analysis of the solutions showed the presence of iron. Neither HCl nor an acid phthalate buffer of corresponding pH produced such coloration.) The air-dried samples were then mixed with 0.1 N sodium hydroxide and the evolved ammonia was determined with a previously calibrated ammonia sensing electrode (Orion #95-10) coupled to an Orion #801 Ion-analyzer. Untreated samples liberated a detectable but insignificant amount of ammonia upon similar base treatment.

Figure 9 shows the separation factors for the various samples.* Clearly shown in the data for the Windsor A horizon and possibly present in the Windsor B horizon data is an apparent change in slope. This may be in-

dicative of different types of sites, associated with the clay and/or organic matter, capable of interacting with the cadmium. The fact that the separation factor is not constant and decreases with increasing coverage indicates that cadmium somehow interferes with its own sorption. It is possible that cadmium which is initially taken up by the soil may block subsequent sorption of cadmium ions. Thus, calcium tends to become more competitive.

Exchange reactions were also carried out using 0.01 N potassium solutions instead of calcium solutions. This resulted in a large increase in separation factors as compared with the calcium-cadmium system. For the Windsor B sample the increased separation factor could be explained on the basis of electroselectivity – preferential uptake of a divalent species in the presence of a univalent ion. For the A horizon the electroselectivity effect was insufficient in explaining the large increase in the separation factor. The higher equilibrium pH's of these Windsor A samples

* For the exchange reaction



where Z_a and Z_b are the charges on species A and B, respectively. The separation factor α_B^A is defined as:

$$\alpha_B^A = (\bar{X}_a X_b) / (\bar{X}_b X_a)$$

where the barred quantities refer to equivalent ionic fractions on the substrate. The molar selectivity coefficient K_B^A is defined as:

$$K_B^A = (C_a^{|Z_b|} C_b^{|Z_a|}) / (C_b^{|Z_a|} C_a^{|Z_b|}).$$

The significance of these two quantities lies in the fact that the separation factor is the best indicator for determining ion preference, even though the preference may be of a purely electroselective nature. The selectivity coefficient is a more fundamental quantity and minimizes electroselective effects. A fuller discussion may be found in Helfferich's book.¹⁴

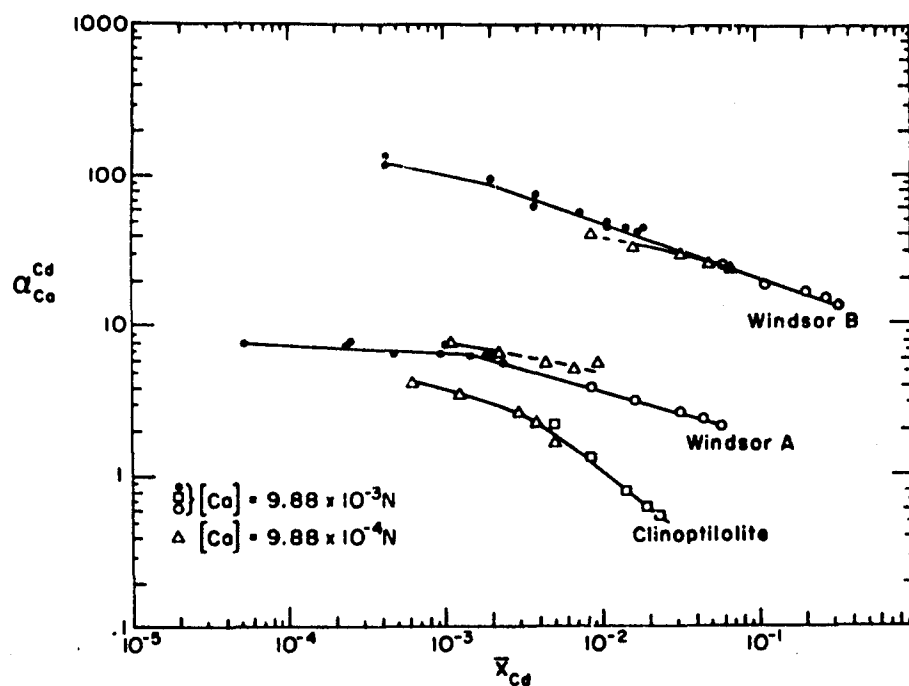


Figure 9. Separation factors as a function of cadmium surface coverage.

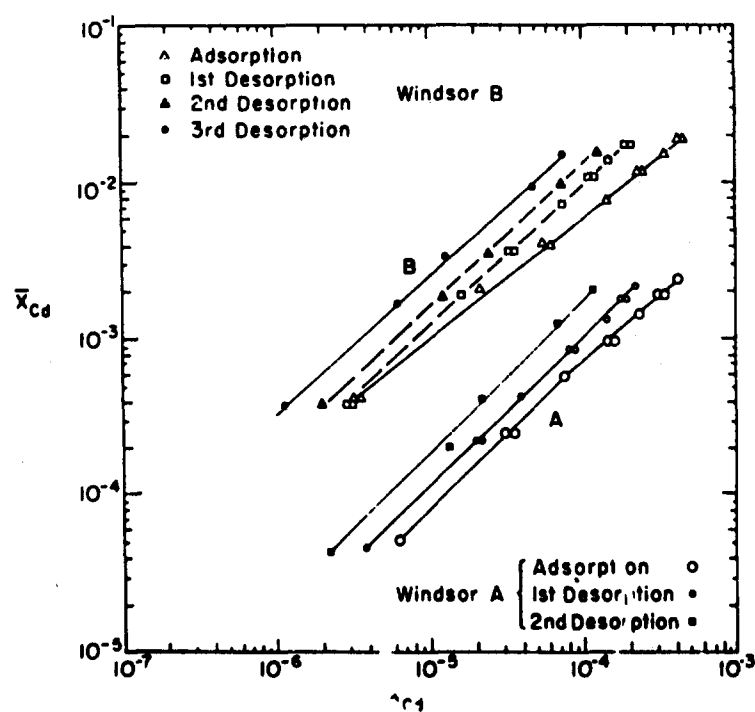


Figure 10. Adsorption and desorption isotherms of alcohol-treated soils. $[Ca^{+2}] = 9.88 \times 10^{-3} N$.

(pH 5.7) and the resultant increase in exchange capacity is not an entirely satisfactory explanation as there would have to have been a four-fold increase in the exchange capacity in the Windsor A sample in order that the results could be explained on the basis of electroselectivity alone.

Reversibility

Earlier work with some of the Charlton soils indicated that even after repeated equilibrations with fresh 0.01 M CaCl_2 to the point where there is no detectable activity in the solution phase, there still existed a significant amount of cadmium associated with the solid phase. This was true even for the one sample of Windsor B.

To ascertain more quantitatively whether the system is reversible, the Windsor A and B samples that are indicated by the open symbols in Figure 6, which had been washed with water and isopropanol and vacuum-dried at room temperature for 48 hours, were mixed with 25 cc of 9.88×10^{-3} N CaCl_2 and allowed to equilibrate for 48 hours. Solution activities were measured and the isotherm was calculated. The samples were decanted, washed and dried, and the process repeated. The results are shown in Figure 10. As can be seen for both the A and B samples the exchange is not reversible. For the B material the first desorption, although showing hysteresis, appears to fall eventually on the adsorption isotherm when the lowest coverage is reached. The second and third desorption isotherms, which are parallel to the first, do not show this effect. The data for the A sample indicate only that the situation is not reversible. It is difficult to reconcile this with the minor increase in pH with increasing desorption steps. With the B sample, unless the ammonium exchange capacities are the result of some specific interaction independent of pH and masking a possible pH dependence of other sites, it would not be justified to assume that pH would have such a marked effect on the adsorption and desorption of cadmium. Likewise, there is no *a priori* reason to suspect that the alcohol treatments have in some fashion altered the system. The arguments for the A sample are similar.

Although several equilibrations with 9.88×10^{-3} N CaCl_2 did decrease the amount of cadmium associated with the soil complex (to 75% of the original amount for the Windsor A and 85% for the Windsor B), equilibrations with either 0.1 N NaCl or 0.1 N NaOH resulted in similar amounts of cadmium being desorbed. Equilibration of the Windsor A samples with 0.1 N HCl reduced the amount of adsorbed cadmium to approximately 5% of the original amount. Two acid equilibrations with a Windsor B sample reduced the amount of adsorbed cadmium to approximately 34% of the original amount.

In order to decide the question concerning possible alteration of the system due to isopropanol, the following experiments were performed. Exchange isotherms were measured in the usual way but in this case the 6-ml aliquot of supernatant liquid which had been removed for counting purposes was replaced by 6 ml of the same CaCl_2 solution used in preparing the initial solutions which were either 9.88×10^{-3} N or 9.88×10^{-4} N in CaCl_2 . These solutions were allowed to equilibrate for 48 hours and the process was then repeated after the 6-ml aliquot had been withdrawn for counting purposes. The results for one Windsor B sample are shown in Figure 11. In a reversible system all points would fall on the same line. The results for the other samples of Windsor A and clinoptilolite were similar.

Use of the separation factor, or any other similar type of coefficient, implies a reversible situation. In the system under discussion the exchange is not totally reversible. It may be the case that the fraction of the cadmium which is behaving as if it were irreversible is in actuality not easily reversible; larger equilibration times may show that the system is completely reversible. However, in light of the previously mentioned leaching data, this does not appear to be the case. Even acid equilibration failed to entirely remove the cadmium on the Windsor B sample. Thus,

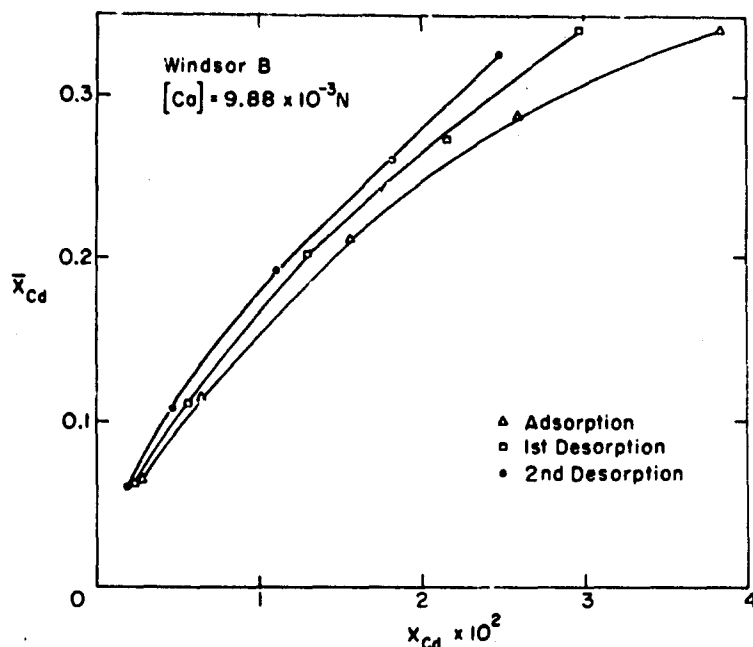


Figure 11. Cadmium desorption on non-alcohol-treated Windsor B.

equilibrium calculations seem to be invalid. However, in practice we are interested initially in α_{Ca}^{Cd} and not α_{Cd}^{Ca} . Thus, the separation factor can be used as a reasonable measure of the efficiency of cadmium removal. The fact that part of the cadmium is no longer easily exchanged is important when considering the fate of cadmium wastewater applied to soil. Leaching of the adsorbed cadmium will be more difficult than indicated by these separation factors.

Conclusions

Cadmium is efficiently adsorbed by two acidic soil horizons in the presence of a relatively large excess of calcium or potassium. The adsorption is not completely reversible and the amount desorbed may possibly decrease with time as isomorphic substitution progresses. Nevertheless, the apparent separation factor provides a good measure of the efficiency of the adsorption. It is fortunate that the adsorption of cadmium in these soils is irreversible, as it will be less likely that this metal will be desorbed in the presence of large amounts of other counterions. The mechanism by which cadmium is held irreversibly is not known; it seems to be unlikely that diffusion into particle interiors has had a chance to become significant over the time frame of these experiments. Clinoptilolite, although of value as an ammonium scavenger in wastewater treatment, has little significance for cadmium removal.

Lagerwerff and Brower,²⁶ using a calcium-substituted Cecil sandy loam, found that, for constant calcium ion concentration, the Gapon coefficient* decreased with decreasing initial cadmium concentration. The Windsor A sample used here is the most comparable to their sample and was found to show similar behavior of the Gapon coefficient but the separation factor increased with

* The Gapon coefficient G for this system as given by Lagerwerff and Brower²⁶ is:

$$\alpha_{Ca}^{Cd} = [\bar{C}_{Cd}(C_{Ca})^{1/2}] / [\bar{C}_{Ca}(C_{Cd})^{1/2}].$$

decreasing concentration. This is mentioned because in this study use of the Gapon coefficient would have led to the conclusion that cadmium selectivity increases with increasing amounts of adsorbed cadmium. Use of the separation factor (or the selectivity coefficient) leads to the opposite conclusion.

The form of cadmium in the soil complex is not known. Data from Butler⁵ indicate that at high ionic strength approximately 20% of the cadmium is in the form of the monochloro complex, CdCl^+ , when the chloride ion concentration is approximately 10^{-2} M. Baric and Branica² have concluded that CdCl^+ is the predominant species in sea water and that the complex species begins to form at chloride concentrations of approximately 0.04 M at the ionic of sea water. If electrolyte sorption is not negligible on various soil types, or in saline soils, it is conceivable that the chloride ion concentration associated with the soil complex might become large enough to influence cadmium adsorption due to the decrease in electroselective preference for univalent ions, such as CdCl^+ , in the presence of multivalent cations.

Suggestions for further research

As previously indicated, the mechanism by which cadmium is bound to the soil is not well understood. Simple cation exchange is relatively temperature independent because of the small heats of exchange. Strongly adsorbed materials may have high heats and thus calorimetric studies may be useful in studying bonding strengths. Similarly, it is known that organic molecules can adsorb onto clay minerals. An investigation of the role such organics play in clay-metal interactions would be highly informative. Isomorphic substitution as a long-term sink for heavy metal removal should be more extensively investigated, perhaps by attempting to detect changes in the mineral phase brought about by long-term association with various metal ions.

Finally, there is some preliminary doubt regarding the correctness of the Gapon coefficient for divalent exchange as reported by Lagerwerff and Brower.²⁶ A complete reexamination of the significance of the various forms of exchange coefficients should be undertaken with the intent of arriving at a uniform description of exchange reactions.

III. THE FLOW OF CADMIUM THROUGH SOILS: AN EXPERIMENTAL METHOD

Introduction

Numerous studies in the area of ion movement through soils have been conducted to gain information useful in both understanding its mechanism and being able to predict such movement in other systems. Invariably laboratory experiments have involved direct analysis, with resultant destruction, of the soil column after an experiment has been performed. This section describes a new nondestructive method whereby the distribution of a metal ion, cadmium in this example, is determined by external scintillation counting of the column following the application of cadmium solutions containing a radioactive "spike." This procedure allows one to perform several experiments on a single column whose physical characteristics remain constant.

Because apparatus design has a bearing on the precision and amount of data obtainable using this method, a description of the apparatus and materials used in development of the procedure is of significance.

Design criteria and detector performance

Apparatus. The apparatus is shown in Figure 12. The Plexiglas columns have an internal diameter of 28.5 mm and a wall thickness of 2 mm. The NaI-Tl scintillation detector is enclosed in a wooden box 12 mm thick and open at both ends. The sides of the unit are encased by 50 mm

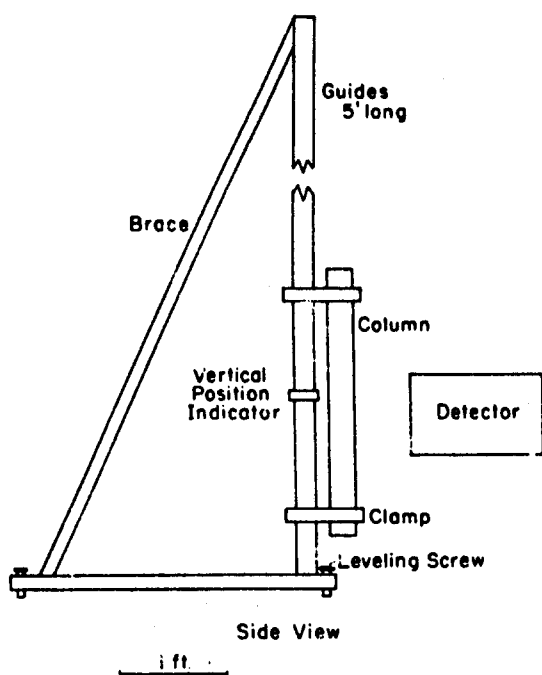


Figure 12. Apparatus used for monitoring cadmium movement in soil columns.

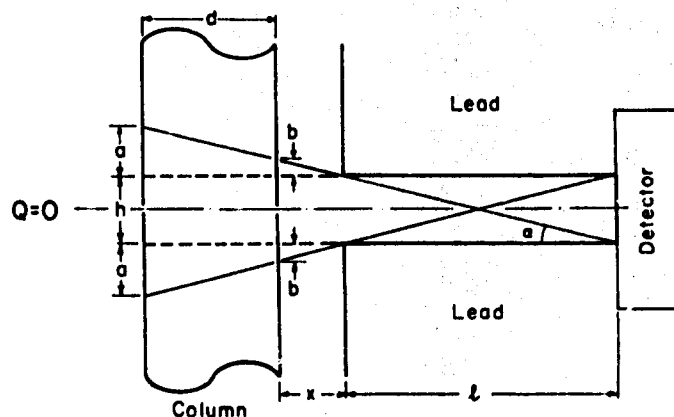


Figure 13. Detector and column geometry. The detector slit is perpendicular to the long axis of the column and sees the entire width of the column.

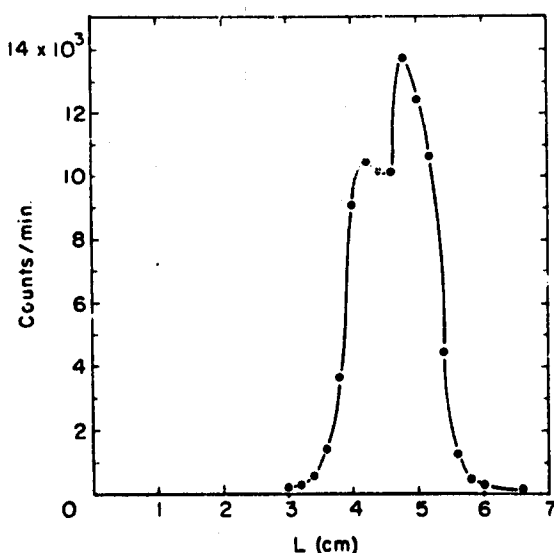


Figure 14. Detector response to two disk sources of ^{109}Cd .

to two disk sources, one having 50% higher activity than the other, that were approximately 9 mm apart in the column. The two peaks can be seen quite distinctly.

If the full width of the column is seen by the detector then the minimum volume element of the column seen by the detector is determined by the slit geometry as shown in Figure 13 and is given by:

$$V = \frac{\pi d^2(a + b)}{8}$$

(1)

of lead, whereas the lead shielding in front is 25 mm thick. A 4-mm-high by 50-mm-wide slit was cut through the front shielding and centered on the detector face. Use of a slit minimizes the counting error by maximizing the number of counts per minute while simultaneously allowing use of a small vertical slit height and thus a higher degree of resolution. The detector itself is a well-type design (Nuclear-Chicago Model #821330) connected to a NC Model #8703 Counter.

The columns, approximately 70 cm long, are mounted on the apparatus and may be moved past the slit. The "spiked" solutions are passed through the column and the column is then "read" on the apparatus.

Detector design. A detailed drawing of the detector geometry, with shielding, is shown in Figure 13. Figure 14 shows the detector response

where

$$a = \frac{h(\ell + x + d)}{\ell} - h, \quad b = \frac{hx}{\ell}.$$

How well a given design approaches this minimum volume element can be determined by passing a plane source, parallel to the detector, past the slit, assuming that the variation of radiation is independent of the distance from the source to the detector (because of the distances involved with the present apparatus this variation is insignificant and need not be considered). In other words, what the detector should ideally see is in direct proportion to the area of the plane source which remains in the geometric field of view of the detector. For a given diameter column, the smaller the volume element the greater the resolution. We define the following parameters (Fig. 13):

- Q = position of the plane source relative to the center of the slit
- I = intensity of radiation reaching detector (proportional to the disk area A)
- I = constant for $Q = 0$ to $Q = (h/2) + b$
- $I = 0$ for $Q > (h/2) + a$
- $I \propto A$ for $[(h/2) + a] > Q > [(h/2) + b]$

The area A of the disk seen by the slit is:

$$A = r^2 \cos^{-1} \left(\frac{r-w}{r} \right) - (r-w) \left[r^2 - (r-w)^2 \right]^{1/2} \quad (2)$$

where

$$w = \left(\frac{h}{2} + a - Q \right) \left(\frac{a-b}{a} \right).$$

The solution, symmetrical around $Q = 0$, is normalized and plotted in Figure 15. Also plotted in Figure 15 is the experimental result for a ^{109}Cd disk moving past the slit. This isotope emits rather low energy photons and provides a source free of many interfering physical phenomena.

As can be seen this assumption approximates the experimental situation but has two noticeable shortcomings. At the maximum it predicts a plateau indicative of constant intensity across the detector face. In reality this plateau is not seen and this is probably due to the fact that the detector is of a well-type design (a flat-faced detector would be much preferred but was not available) and thus would impart some inhomogeneity into the situation. At the extremes of the detector's geometric viewing angle it can be seen that the radiation has not dropped as rapidly as predicted. This is possibly due to scattering of some of the radiation off the slit walls and/or some radiation reaching the detector after having passed through the lead.

An analytic solution capable of describing this situation would be exceedingly difficult to obtain and its usefulness is questionable. For example, in attempting to determine the cause of the slow drop-off in intensity at the extremes of the detector's acceptance angle, it would be necessary to know the mass absorption coefficients of the photons emitted by, in this case, cadmium in lead. These coefficients are not known with certainty but can be estimated from tables.⁷ However, these values are based on "good geometry," where the source is distant from the shielding. The effective absorption coefficient decreases as the geometry becomes poorer, as is the case with this apparatus. This consideration, along with the fact that 1) there is total attenuation if the slit is replaced by solid lead (indicating that so-called "buildup" is negligible), and 2) the response of the probe is unaffected, except at the maximum, by the presence of a standard aluminum absorber

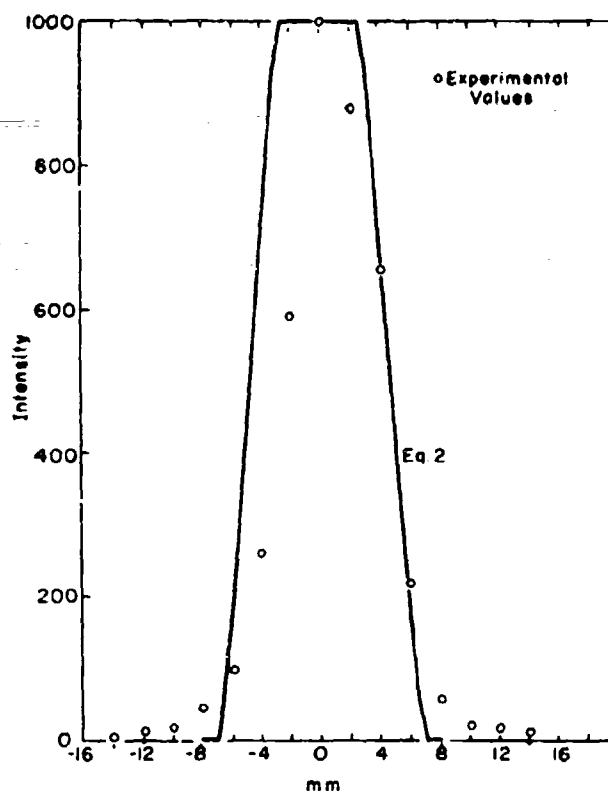


Figure 15. Comparison of experimental values for a disk source of ^{109}Cd moving past slit with theoretical response predicted by eq 2. The intensity is in arbitrary units.

(605 mg/cm³) placed between the detector and the slit (to filter out scattered lower energy photons) tend to support the premise that in this particular case the "extra" photons are passing through some of the lead and reaching the detector. The situation becomes even worse when sources such as ^{22}Na are used that emit higher energy photons. Here, scattering of high energy photons within the lead becomes significant. These scattered photons are, however, of lower energy. Further discussions of these problems are found in Fitzgerald et al.¹⁰

The best results would probably be attained using a counter with an attached pulse height analyzer so that the photon energy giving the smallest "window" commensurate with a statistically significant counting rate could be utilized. Use of a flat-faced detector is also preferable.

The next section deals with various methods of analyzing the measured profile and attempting to relate it to relative distribution of isotope in the column.

Mathematical analysis of curves

As mentioned previously it might be possible to develop the preceding section to the point where the actual distribution of the isotope within the column could be determined exactly. However, there are other methods which do not require the assumptions and approximations involved in such calculations.

What is actually seen by the detector is a "smoothed" profile, or one that has been convolved with a set of experimental "weights." Healy¹¹ discusses this in detail but a short explanation will be presented here. Suppose a column has at three adjacent levels isotope activities of 1, 1 and 1. The detector does not see just one level of the column but several levels due to the size of the acceptance angle. And it sees these levels at varying efficiencies, i.e. the effect of the portion of the soil column that is centered on the detector is larger than the effect of the portions above and below this central point. Suppose that the detector can see all three levels at once but it sees the central level three times more efficiently than either of the other two levels. In other words, the detector assigns weights of 1, 3, 1 to the readings. The data thus become convolved or smoothed as shown:

<u>Level</u>	<u>Actual strength</u>	<u>Smoothed values</u>
0	0	1
1	1	4
2	1	5
3	1	4
4	0	1

The smoothed values are obtained by aligning the central weight, 3, at any level, cross multiplying the product and adding the resultant values. For example, at level 2:

<u>Level</u>	<u>Actual</u>	<u>Smoothed</u>
0	0	
1	1 × 1	
2	1 × 3	5
3	1 × 1	
4	0	

The general expression for this smoothing is:

$$E_L = \sum_{k=-(N-1)/2}^{(N-1)/2} w_k T_{(L+k)} \quad (3)$$

where E_L is the smoothed value at the L th level, T the true value, w_k the k th weight, and $T_{(L+k)}$ the true value at position $L+k$, all for N weights. If the experimental conditions are such that it is known that all true values are zero at points beyond the end points, then for N weights, E experimental values and T true values it is apparent that

$$T = E \cdot N + 1.$$

Implicit in all these methods is the fact that there is a central weight (i.e. the total number of weights is odd) and that the data are equally spaced, with the spacing identical to the weight spacing. Equation 3 can naturally be inverted (deconvolution) in order to solve for the true values, given the experimental values and the weights. The difficulty with solving the problem using the deconvolution method is that it is highly sensitive to random errors (noise) and, because we start evaluating the true values at one end point and calculate through to the other end point, this error is propagated and gets increasingly larger as each unknown value is subsequently evaluated. This turns out to be the situation with the counting data since the values are inherently noisy.

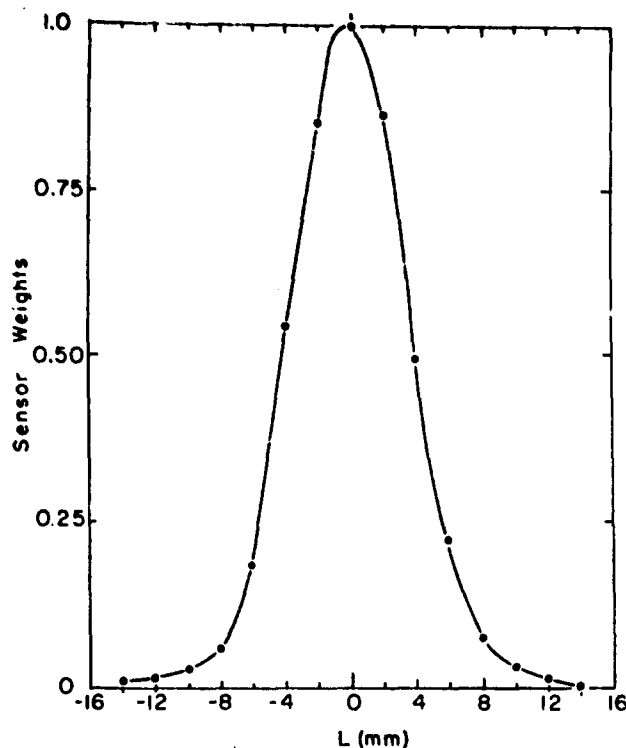


Figure 16. Sensor weights as determined by passing disk sources past slit.

Cox,⁶ using a similar experimental arrangement in his investigations of sea ice, solved the equations simultaneously. Equation 3 may obviously be arranged in a matrix format. For N weights there will be $(N - 1)$ extra equations. In addition, there is one more equation available:

$$K = \text{constant} \quad T_1 + T_2 + T_3 + T_4 + T_5 + \dots + T_N. \quad (4)$$

In order to solve for the unknowns by matrix inversion N equations must be eliminated. Analysis of experimental data using this technique was not satisfactory because no equation is better than any other and all the equations have not been utilized. In addition there is some error in the computer's inversion process which may increase the error in the calculated true values. Random error in the experimental values is probably the predominant source of error in analysis by this method.

There remains one final method to be discussed here. Before doing so it will be advantageous at this time to discuss how the sensor weights were determined. Three disk sources of ¹⁰⁹Cd, each having a different level of activity, were placed parallel to the detector. They were moved past the detector in 2-mm increments and the number of counts per minute was recorded at each level. Because the "window" sizes were identical, the results were normalized to the lowest activity (0.133 μ C) and averaged. The results are shown in Figure 16. By dividing each value by the maximum value one obtains a set of weights which reflect the significance of each level to the total counting rate at the central level. The sum of the weights is called the gain and for this system was equal to 4.4. A total of 15 weights are involved.

As indicated by Healy,¹³ and discussed at length by Holloway,¹⁷ any curve can be described by using Fourier transform analysis. An experimental profile (see Figure 20 for example) consists of a steeply rising portion due to the detector approaching the soil/air interface and a more gently sloped decreasing portion as the isotope trails off in the lower part of the soil column. The effect of the sensor is to smooth the true profile such that the high frequency components of the steeply rising portion are suppressed. The problem is therefore to undo the damage done by the smoothing process.

The sensor's frequency response $R(f)$ is defined as:

$$R(f) = \sum_{k=-n}^m w_k \cos(2\pi f k) + i \sum_{k=-n}^m w_k \sin(2\pi f k). \quad (5)$$

There are $(n + m + 1)$ weights (w_k); f is the frequency or cycles per data interval, and is allowed to vary between $0 \leq f \leq 0.5$. If $w_{-k} = w_k$, then the sine term vanishes and the function is said to be even. For non-vanishing sine terms the value of $R(f)$ is defined as the square root of the sum of the squares of the real and imaginary parts:

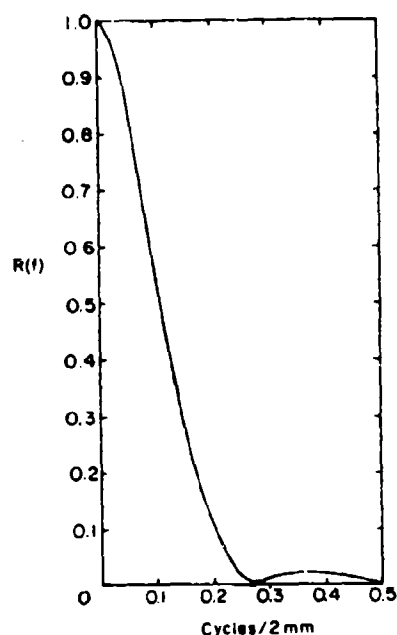


Figure 17. Frequency response of sensor weights as calculated by eq 5 and 6.

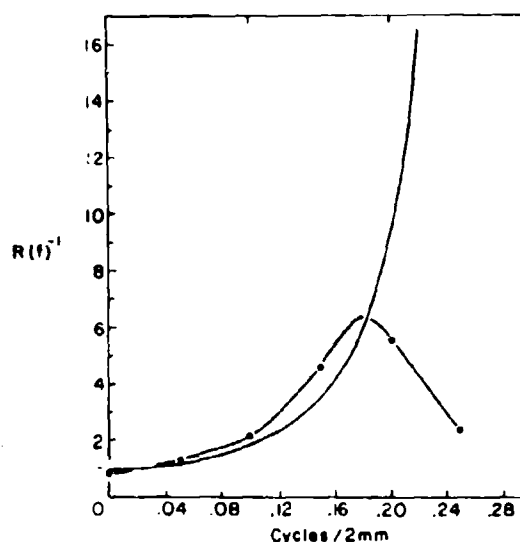


Figure 18. Inverse frequency response of sensor weights (continuous line). The points represent an attempted filter design as described in the text.

$$|R(f)| = (|\text{Re}[R(f)]|^2 + |\text{Im}[R(f)]|^2)^{1/2} \quad (6)$$

By utilizing eq 5 and 6 the frequency response $R(f)$ of the sensor weights is obtained and is plotted in Figure 17. More importantly, since we will be interested in reversing the procedure, the inverse frequency response $R(f)^{-1}$ is obtained and is plotted in Figure 18.

The problem is to find a suitable filter that will amplify the frequencies which have been suppressed. This was initially done by convolving the $R(f)^{-1}$ values at 0, 0.05, 0.10, 0.15, 0.20 cycle with a filter having weights of 0.25, 0.5, 0.25 (Fig. 18). As discussed by Hibler¹⁶ such a smoothing reduces spurious ripples in the filter's frequency response. The resultant values were found to be unsuitable in the low frequency range so that it was necessary to arbitrarily select non-smoothed values:

<u>Frequency</u>	<u>$R(f)^{-1}$</u>
0	1
0.05	1.15
0.10	1.75
0.15	3.4
0.20	5.55
0.25	3.5
0.30	1.35
0.35	1
0.40	1
0.45	1
0.50	1

This is not the most desirable method of selection but was found to suffice for the situation here. The best method is to generate the desired values of $R(f)^{-1}$ by convolving the original values of $R(f)^{-1}$ with a smoothing function. In either case, it is necessary to reduce $R(f)^{-1}$ at high frequencies from the ideal value since too much amplification results in amplified noise (error). Consequently, in practice we are not able to restore the highest frequencies.

If it is now assumed that the function is even, i.e. the weights are symmetric about the origin, then one can solve for the weights that will generate this inverse frequency response. Using Hibler's¹⁰ notation, but with a slightly different form of his eq 2:

$$w_k = \frac{R_0}{2N} + \frac{R_N \cos(2\pi k f_N)}{2N} + \frac{1}{N} \sum_{l=1}^{N-1} R_l \cos(2\pi l k) \quad (7)$$

where R_l is the inverse frequency response at frequency l and

$$N = (\text{no. of weights} - 1)/2.$$

For this situation $N = 10$ (i.e. the weights are symmetrically distributed around the central weight at R_0), and the equation is designed to return weights with unity gain. Since the original set of sensor weights has a gain of 4.4, these new weights are divided by this value. The sensor weights could just as easily have been unitized previously.

The test of the validity of this method is shown in Figure 19. Theoretical true profiles have been convolved with the sensor weights to obtain an "experimental" curve. These curves have then been convolved with the filter weights determined from eq 7 to regenerate the original profiles. As can be seen, the agreement is quite satisfactory except at the very beginning, which is probably indicative of the imperfection of the filter. Because the sensor eliminated the very high frequency components we will always be faced with the problem of determining the end point. It may be determined by trial and error: by finding the point that when combined with the others and then convolved with the sensor weights regenerates the experimental profile most closely. Alternatively, we may make use of eq 4 to solve for this value or utilize the fact that the area under the experimental curve is 4.4 times that of the true profile to calculate the missing point.

Use of this filter on an actual experimental profile is shown in Figure 20. As can be seen, the calculated true profile, when convolved with the sensor weights, generates the experimental profile. Here, by trial and error, the fourth guess led to the decision that the true end point lies at the position indicated. These results give a reasonable experimental profile upon recalculation. The choice of any reasonable end point results in little or no influence on the descending part of the curve for a slit with narrow resolution or for the end point sufficiently far removed from the descending part of the curve.

Figure 21 shows the results for a series of experiments. The experimental conditions were as follows: 500 g of < 2 mm calcium-saturated Windsor B soil was packed dry into a column in order to minimize stratification of the soil. Visual observation indicated minimal detectable banding. The resultant bulk density was approximately 1.4 g/cm³. The column was evacuated and filled with distilled water. A minimal amount of solution was always maintained over the top surface to prevent air from entering the soil column. Solutions with volumes no larger than 50 cc were passed through the column at a constant rate of 0.06 cm/min. Readings were taken shortly thereafter or as indicated. Proper end points have not been calculated for these curves as we are mainly interested in the descending portions. The curve (Fig. 21) with the plateau preceding the maximum is a case where there is approximately one centimeter of standing isotope solution on the surface.

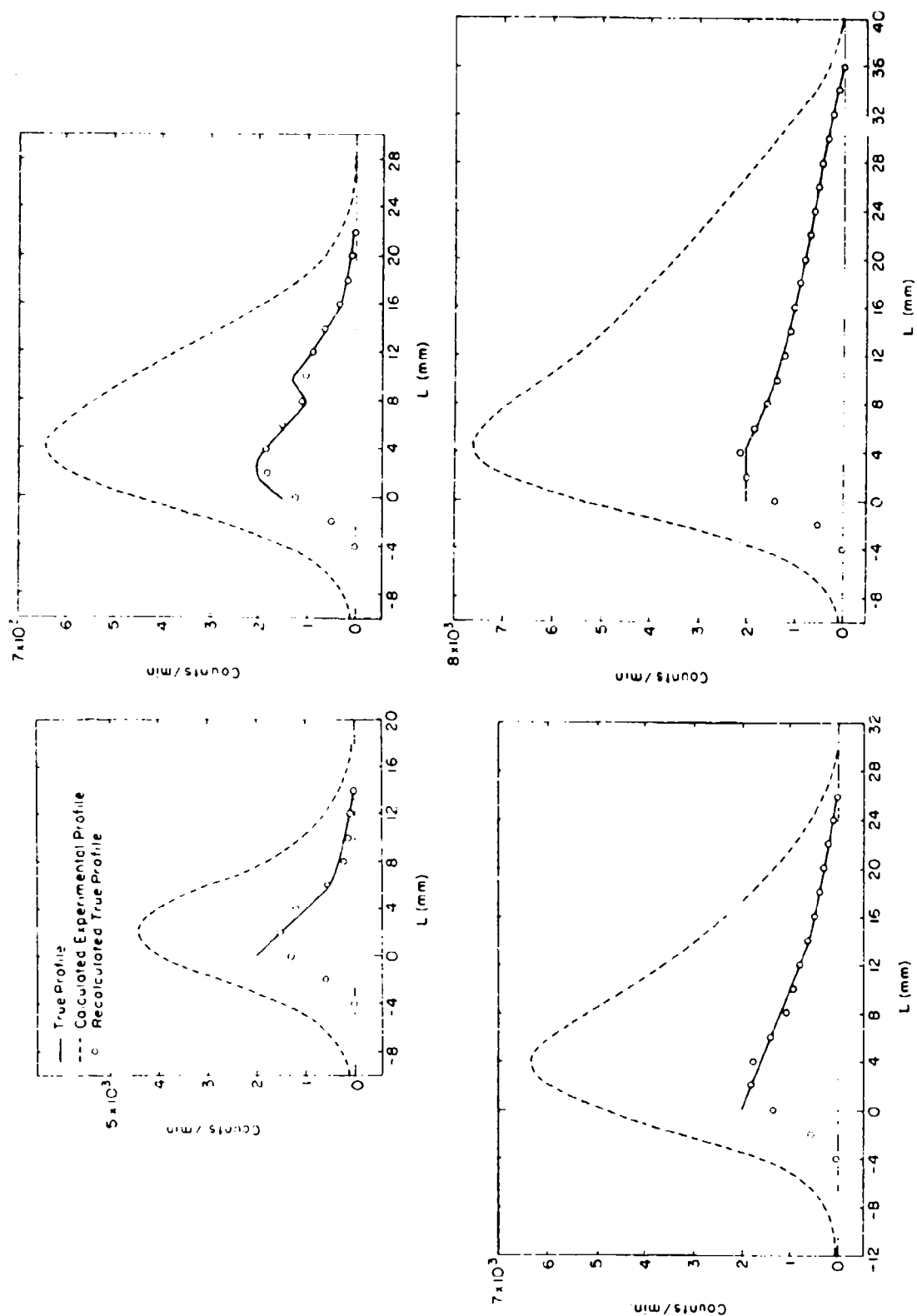


Figure 19. Calculated examples of filtering technique. An arbitrary true profile was drawn and these values then convolved with the sensor weights to show what the experimental profile would look like. These values were then convolved with the filter weights determined using eq 7 to regenerate the new estimate of the true profile.

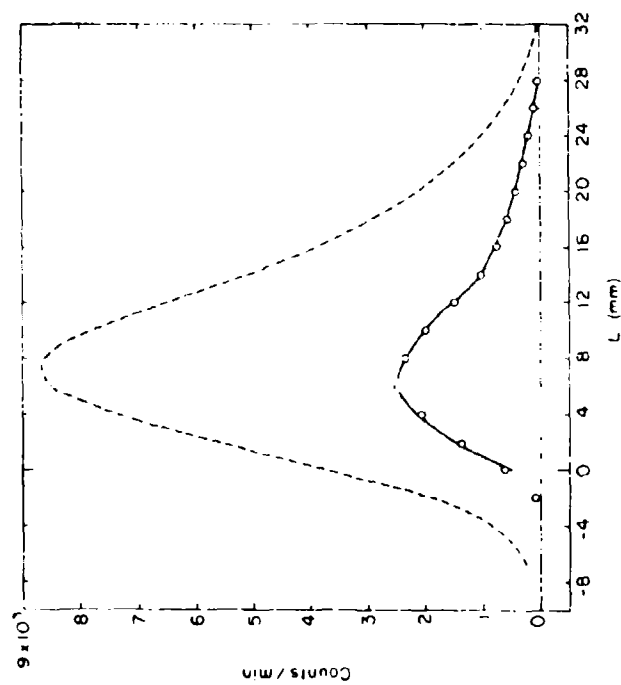
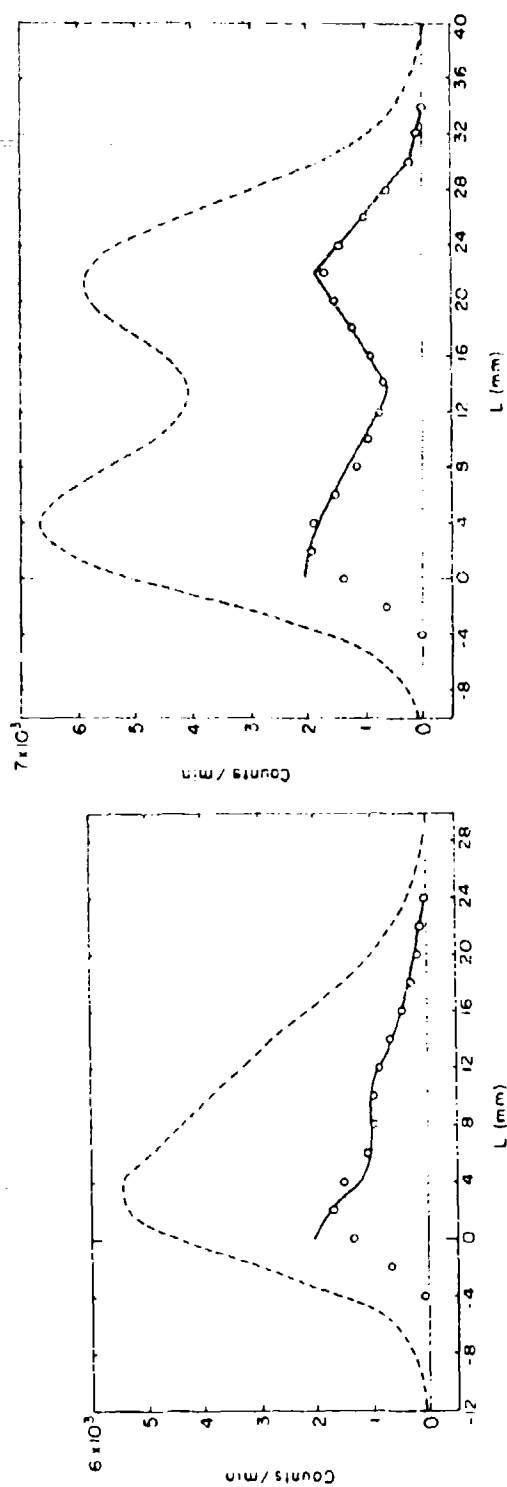


Figure 19 (cont'd)

SORPTION OF CADMIUM BY SOILS

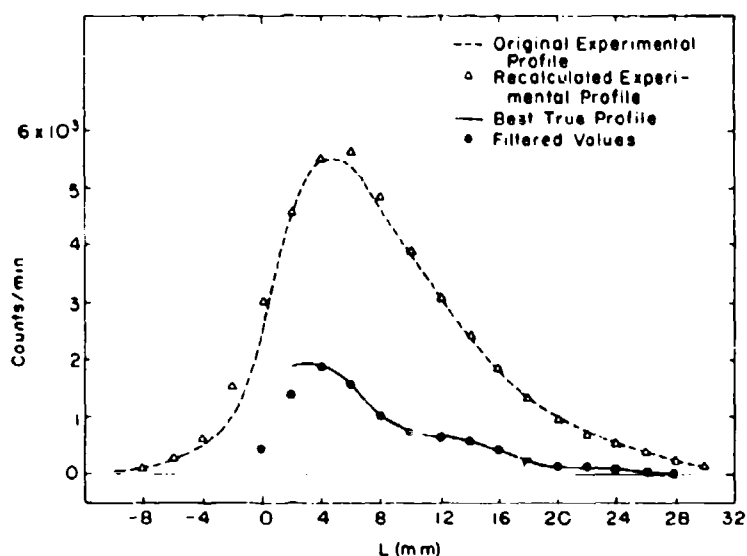


Figure 20. Actual experimental profile and calculated true profile.

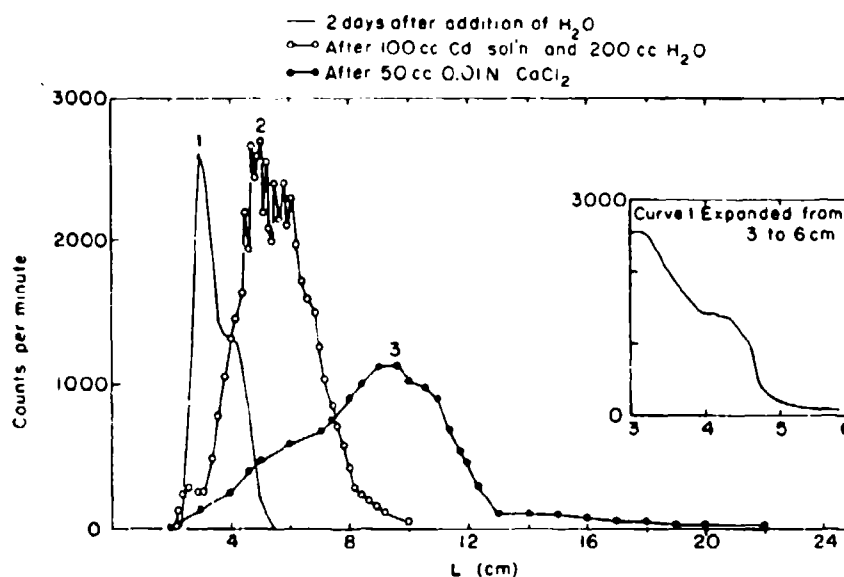


Figure 21. Calculated true profiles for a Windsor B sample. Already present in the system for curve 1 are 100 cc of CdCl_2 , ($[\text{Cd}^{+2}] = 7.88 \times 10^{-4} \text{ N}$). After the system had stood for four days 50 cc of H_2O were added and the column counted two days later.

The existence of a plateau on the descending portion of the profiles can in some cases be seen, to a smaller extent, in the original experimental profile where it appears as a shoulder on the descending portion of the curve. Whether it is a physical error, due to some form of flow maldistribution, or a true situation, due perhaps to the presence of CdCl^+ , is not known. Non-equilibrium distribution seems unlikely as the plateau is seen even after several days. No further interpretation of the data will be made here except to note that curve 3 of Figure 21, representing the results of calcium chloride addition, is very similar to that of the original profile. This is due to a combination of the narrow slit resolution and the small slope angles. This will not necessarily be the case when high energy isotopes are used.

Curve 2 of Figure 21 represents an interesting situation, the exact cause of which is not known. Oscillation has been introduced which may be due to either a peculiarity of the data used in the calculation or to the fact that non-smoothed values of $R(f)^{-1}$ were used to calculate the weights. The actual experimental profile did show a slight depression at its maximum. The areas under experimental curves 2 and 3 were identical within experimental error.

Conclusions

The use of a filtering function is seen to be useful in decoding convolved profile data obtained by the previously described methods. Problems exist in the high frequency region but can be corrected for, and excellent agreement is obtained in the low frequency region (the descending part of the curve). The latter is of more interest from a theoretical standpoint.

The method is quite general and should work with other system geometries and other isotopes whose photon energies are so high as to give poor resolution.

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